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Application of ion sensitive field effect transistor (ISFET) for the analysis of soil pH, nitrate and available potassium

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Abstract

This paper describes the application of ISFET technology in analyzing the soil sample and correlating it with the convectional soil testing method. These devices can offer sensitive, selective, reliable, and often cheap measurements for an ever increasing diversity of sensing requirements. These sensors are procured from Microsens, Switzerland and the circuitry of ISFETs was made with the help of Elico Pvt Ltd. The experiment setup was done in ICAR-IISS, Bhopal. The soil sample were of the order Vertisol, Inceptisol and Alfisol and its analysis for soil pH, nitrate and available potassium was performed through ISFET. Also covering the conditioning and calibration procedures for ISFET. Furthermore limitation of ISFET of ISFET regarding linearity range, drift and sensitivity have been discussed. The reported sensitivity for obtained was 56.8mV/decade, 34mV/decade and 60mV/decade for pH, Nitrate and potassium respectively. The correlation results with convectional method was significant in case of pH with $R^2 = 0.95$. On the other hand nitrate and potassium showed $R^2 = 0.59$ and 0.63 respectively in which further improvement is needed.

Keywords: Ion sensitive, ISFET, nitrate and available potassium

Introduction

Modern agriculture demands continuous information of chemical and physical soil parameters, which is not timely available with traditional techniques. Conventional soil testing methods are costly and time consuming because they require complex processes for pre-treatment and expensive instruments for samples to be quantitatively analyzed. In today's scenario electro chemical sensors are transforming our lives. These devices can offer sensitive, selective, reliable, and often cheap measurements for an ever increasing diversity of sensing requirements.

Sensors have been used to measure many chemical properties including pH, conductivity, salinity, potassium, nitrate, and phosphate as these sensors are generally more robust and versatile and they can achieve high sensitivity with short response time. However, if these sensors are to be used in soil testing, they need intensive and complex laboratory testing against already accepted methods which are already calibrated for fertilizing the crops. Electrochemical sensing uses ion-selective electrodes or ISFETs to generate a voltage or current output in response to selected ions and their activity in the solution, while biological sensing uses a nutrient-sensitive layer of immobilised enzymes deposited on to an electrode or electrochemical cell to observe the reaction between the nutrient of interest.

An ion selective field effect transistor (ISFET) is a field-effect transistor used for measuring ion concentrations in solution; when the ion concentration (such as H^+ , see pH scale) changes, the current through the transistor will change accordingly. This was invented in 1970. An ISFET is essentially a metal oxide semi-conductor field effect transistor (MOSFET) with the metal gate electrode replaced by an insulator layer, such as silicon nitride, acting as a barrier covered with a chemically sensitive structure, consisting of an ion- sensitive membrane or layer, and is used in conjunction with a reference electrode. It acts as a transducer with the ion-sensitive membrane converting the chemical activity of an analyte species into a potentiometric response, whilst the FET part converts this into a change in the drain current flowing through the device. Here, the solution is used as the gate electrode. A voltage between substrate and oxide surfaces arises due to an ion sheath.

It is a special type of MOSFET, and shares the same basic structure, but with the metal gate replaced by an ion-sensitive membrane, electrolyte solution and reference electrode.

In this work, the use of chemical sensors based on ion sensitive field effect transistors (ISFETs) for soil analysis is proposed. These devices are fabricated with microelectronic technology – providing some important advantages such as robustness, small size, low output impedance and mass production. In this work, the ISFETs for pH, NO₃⁻ and K⁺ with polymeric membranes were tested in aqueous solutions, each of the parameters analyzed through ISFETs was tested against the standard laboratory procedures.

Method and Material

The experiment was setup in laboratory of Soil fertility and chemistry division, ICAR-IISS, Bhopal (M.P.). ISFETs were procured from Microsens, Switzerland. The circuitry of ISFETs was made with the help of Elico Pvt Ltd. The software for the analysis was loaded in the laptop. The experiment comprised of three soil type i.e. Vertisol, Inceptisol and Alfisol, whose samples were collected from southern and Northern parts of India. Five samples from each soil type were taken with three replication. The statistical analysis was done through paired t-test, comparing the means of results obtained through convectional soil testing method and ISFET.

For the convectional soil testing method the pH of soil was determined by the method described by Piper (1967). Soil was shaken with water (1:2.5), and the pH was measured on a pH meter. Nitrate was determined by automated cadmium reduction method as described by Baird and Bridgewater (2017). Three 3g of air dried soil was mixed with 30 ml of 2 M KCl and shaken for 1 h on a mechanical shaker. The soil suspension was filtered into 100 ml beaker and then was determination for NO₃-N using the auto-analyzer/ flow injection analyzer. The available potassium was extracted (1:5 soil to extractant ratio) from the soil by 1 N neutral ammonium acetate and analyzed by flame photometer as described by Hanway and Heidal (1952).

ISFET Conditioning and Calibration

Before the first use or extended periods of drying, conditioning and calibration of ISFET sensor is recommended. The conditioning buffer is specific for each ISFET sensor element which was conditioned for 6-12 h period of time before the calibration process. The conditioning buffer contains 10mM of KCl for K⁺ ISFET, 10mM of NaNO₃ for NO₃ ISFET, the pH ISFET sensor can be conditioned in Cl⁻ ion containing buffer solution. The reference electrode also needs to be conditioned in 0.1 – 1M KCl solution for 12-24h (for PVA based electrode). The impedance of the dry electrode is very high and will decrease after conditioning.

Regular calibration was recommended in order to correct the baseline values. Depending on the required precision, a one-point measurement can be sufficient, since the ion sensitivity

of the functionalized sensor changes much more slowly than the baseline values. Calibration of each sensor was done with the dedicated calibration buffer solution. The calibration buffer solution consist of primary ion concentration (K⁺ and NO₃⁻) in desired concentration (5*10⁻⁴ -0.1M). A background buffer based on intended application was applied to the primary ion concentration. For the pH calibration, standard buffer of pH 4, 7 and 10 was used. Nitrate standard solution was prepared with the primary ion sodium nitrate and was diluted in the background buffer sodium chloride solution with the concentration range of 1 mM to 100 mM similarly, potassium chloride was taken as primary ion diluted in sodium chloride as background buffer for potassium standard preparation. Other background buffer used for potassium was ammonium acetate (5*10⁻⁴ - 0.1M).

Soil analysis through ISFET

For the soil analysis through ISFET, convectional soil testing procedures were followed i.e. for pH 1:2.5 soil to extractant ratio, for nitrate automated cadmium reduction method as described by Baird and Bridgewater (2017) and for potassium 1 N neutral ammonium acetate analyzed by flame photometer as described by Hanway and Heidal (1952).

At this time the 'samples' being analysed was the pure extraction solutions. The first few injected samples consisting of a mixture of soil extract and the pure extractant solution were analysed in the case of nitrate and potassium. For pH soil suspension was used to determine the pH. The ISFET took longer response time period as claimed in our experiment, the average time for a result was 5 minute and maximum 15 minute time.

ISFET Sensitivity, drift and linearity range

The sensitivity of the ISFET element is specific for the sensor type. The pH ISFET sensor have the maximum attainable sensitivity with 55 mV/pH unit. For nitrate and potassium the sensitivity is reached up to 47 (±4) mV/decade and 50 (±4) mV/decade respectively operating at the temperature 0 °C - 45 °C. Furthermore, the drift rate of Ta₂O₅ and Al₂O₃ ISFETs is only, 0.1-0.2mV/h. Tantalum pentoxide ISFET shows significant light-induced drift. This drawback limited the applicable range of Ta₂O₅ sensing membrane, and many research groups are using different fabrication processes and post-annealing treatments to solve this problem. The working range for the Microsens ISFET is 5*10⁻⁴ - 0.1M, though at the lower range the required sensitivity was not achieved.

Results

Calibration of ISFET

Coefficient of determination (R²) and sensitivity (mV per decade) of various standard curves for ISFET Artigas *et al* (2001) [2] reported a sensitivity of 55.7, 54.1 and 62.6 mV per decade for K, pH and nitrate, respectively using ISFETs. They also reported a linear range of 7 x 10⁻⁵ to 0.1, 2 to 12 and 2.3 x 10⁻⁵ to 6 x 10⁻² M for K, pH and phosphate, respectively.

Table 1: Coefficient of determination and sensitivity (mV per decade) of various standard curves

S. No.	Parameter	Medium	R ²	Sensitivity (mV per decade)
1	pH	Buffers 4.0, 7.0 and 10.0	1.000	56.8
2	Nitrate	i. Sodium nitrate	0.996	34.5
		ii. Sodium nitrate + sodium chloride	0.989	25.5
		iii. Sodium nitrate + potassium chloride	0.997	24.0
3	Potassium	i. Potassium chloride	0.988	23.5
		ii. Potassium chloride + sodium chloride	0.994	60.0
		iii. Potassium chloride + ammonium acetate	0.999	32.5

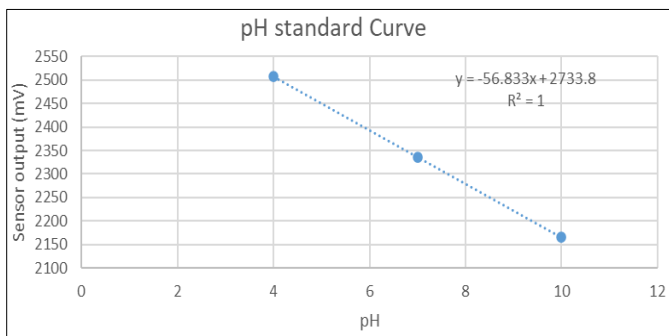


Fig 1: Standard curve for pH using buffer solution of pH 4, 7 and 10

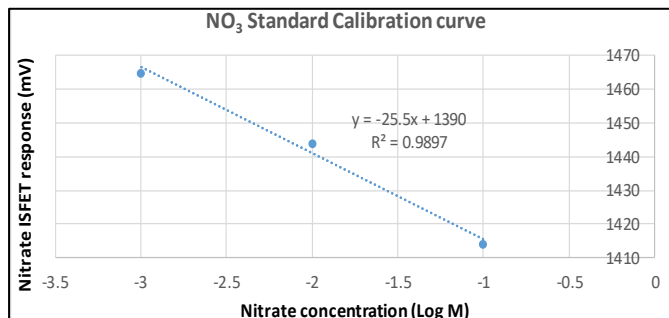


Fig 2: Standard curves for nitrate prepared through sodium nitrate + sodium chloride

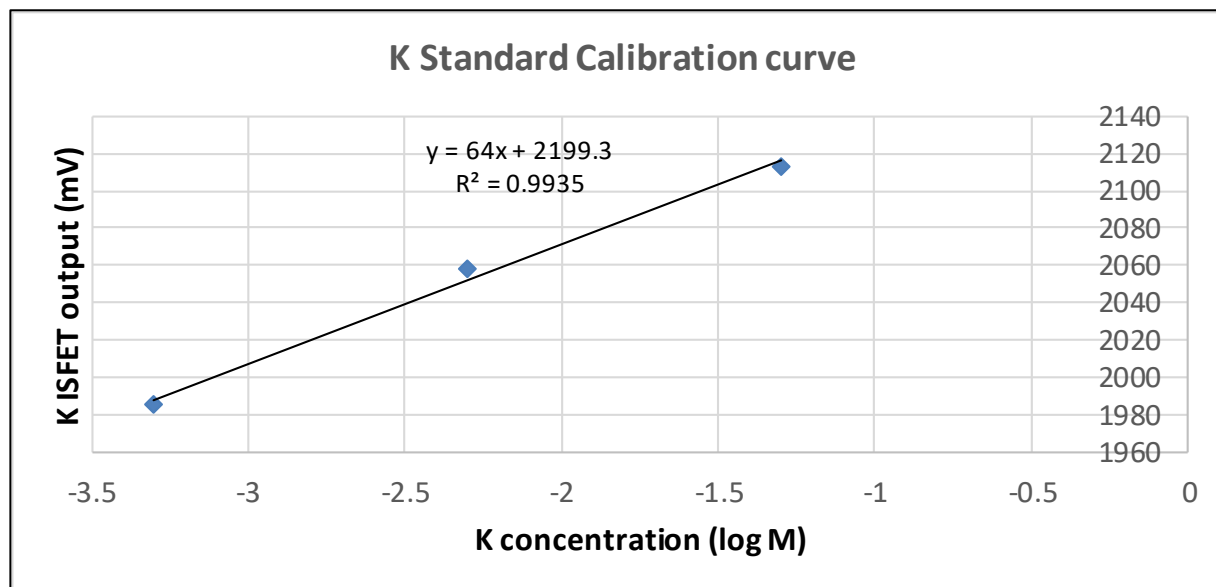


Fig 3: Standard curve for potassium prepared potassium chloride + sodium chloride standard

Soil analysis through ISFET

Soil pH: Soil samples were compared where the pH (1:2.5 soil: water) was determined by ISFET and pH meter and the results are shown in table 2. The results of the paired t test

represent a P (0.05) value of 0.865 which shows to accept the null hypothesis that there is no significant difference in the mean pH values of ISFET and pH meter. The results show significant correlation with $R^2 = 0.95$

Table 2: Estimation of soil pH through ISFET and pH meter

S. No.	Soil	pH (ISFET) (Mean of three replications)	pH (pH meter) (Mean of three replications)
1	Hisar-2	7.9	8.1
2	Periyanaickenpalayam (110+)	7.7	7.6
3	Pura (36-100)	7.1	7.1
4	Kakara (39-81)	7.2	7.2
5	Khadar (B1)	7.5	7.4
6	Pomberty (32-49)	8.4	8.4
7	Sarol (54-95)	8.1	8.0
8	Kamliakheri (21-38)	7.8	7.8
9	C-24 (black soil)	7.8	7.8
10	C-25 (black soil)	7.7	7.6
11	P-40 (black soil)	7.8	7.8
12	Q-15 (black soil)	8.3	8.2
13	Kodad (40-65)	7.3	7.2
14	Patancheru (10-20)	6.3	6.2
15	Palathurai (15-38)	7.8	7.8
	Mean	7.6	7.6
	Paired t test (P=0.05) = 0.865		

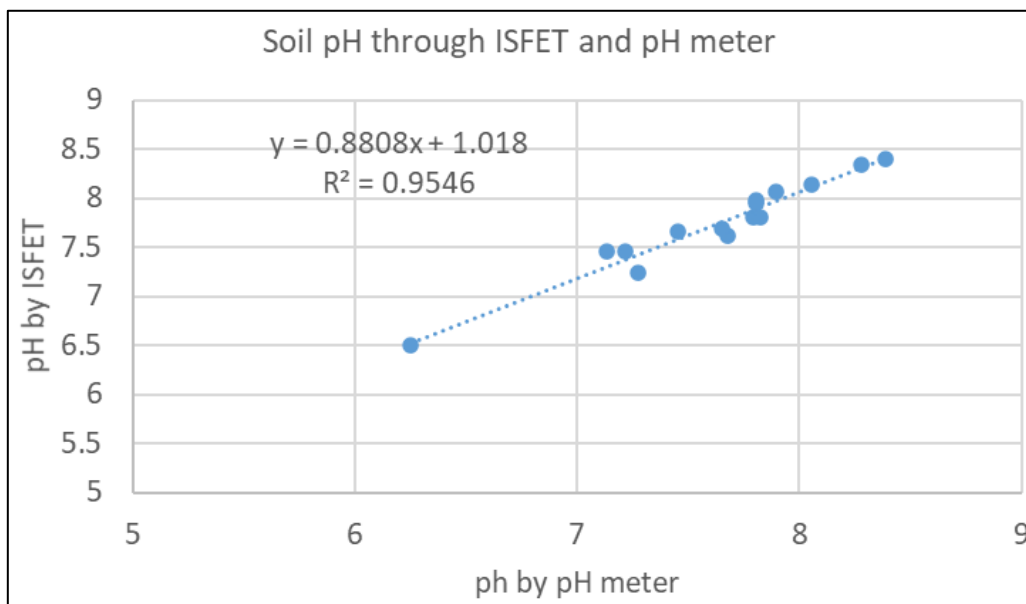


Fig 4: Comparison between Soil pH through ISFET and pH meter

Nitrate

The sensitivity of nitrate was -34.5, -25.5 and -24.0 mV per decade for calibrations prepared in sodium nitrate, sodium nitrate + sodium chloride and sodium nitrate+ potassium chloride, respectively. The range of linearity in the prepared calibration curves was 1 mM to 100 mM. However, a linearity range of up to 0.5 mM nitrate for the ISFETs used in our experiment has been reported. Birrel (2001) [5] reported a regression slopes (sensitivity) of for ISFET at -22.8, -24.4, -26.6, and -25.2 mV/decade for the concentration ranges 0.05–0.2, 0.07–0.2, 0.07–1.0, and 0.07–10.0 mM NaNO_3 , respectively. An interference of Cl^- is reported in the literature during nitrate estimation with ISFET since for electrochemical reactions chloride and nitrate behave similarly. In our results, however, no interference of chloride ions could be observed and we could draw good calibration curves in the presence of chloride.

Comparable results were obtained in the two methods. The results of the paired t test also indicate that there is no significant difference the mean of two results.

Table 3: Estimation of nitrate through ISFET and FIA (Mean of three replications)

S. No.	Soil	Nitrate (ISFET) (mg/kg)	Nitrate in FIA (mg/kg)
1	Hisar-2	55.0	18.4
2	Periyanaickenpalayam (110+)	11.8	10.0
3	Pura (36-100)	25.5	24.8
4	Kakara (39-81)	13.0	12.4
5	Khadar (B1)	30.9	29.4
6	Pomberty (32-49)	30.9	42.3
7	Sarol (54-95)	80.7	56.8
8	Kamliakheri (21-38)	55.0	47.7
9	C-24 (black soil)	41.2	44.4
10	C-25 (black soil)	41.2	49.1
11	P-40 (black soil)	88.9	41.3
12	Q-15 (black soil)	50.0	27.5
13	Kodad (40-65)	10.8	6.9
14	Patancheru (10-20)	8.1	5.8
15	Palathurai (15-38)	5.5	1.9
	Paired t test (P=0.05)= 0.063		

FIA: Flow Injection Analyser

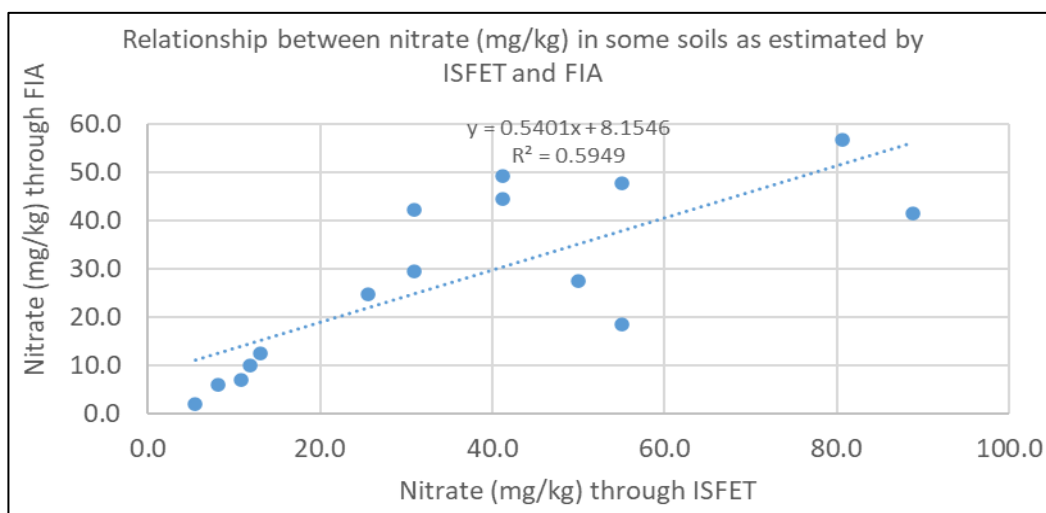


Fig 5: Relationship between nitrate (mg/kg) estimated by ISFET and FIA

Potassium

The sensitivity obtained through calibration was 23.5, 64.0 and 32.5 mV per decade for potassium chloride, potassium

chloride + sodium chloride and potassium chloride + ammonium acetate respectively. Stuart (2006) reported typical slopes of 54.6 to 58.2 mV per decade change in

activity of potassium ion when the KCl concentrations were above 10^{-5} mole/L. Comparatively, potassium result show better results than the nitrate samples. However, outliers can be seen in the results which was probably due to potential drift, interfering ions (such as Na^+ and Cl^- ion). Adamchuk

(2002) [1] reported that it was feasible to determine K content of moist soil samples ($r^2 = 0.56-0.94$) if limitations such as inconsistent contact between soil and electrode and potential drift due to continuous measurements were addressed.

Table 4: Estimation of potassium through ISFET and Flame Photometer (Mean of three replications)

S. No.	Soil	Potassium (ISFET) (mg/kg)	Potassium Flame Photometer (mg/kg)
1	Hisar-2	137	123
2	Periyanaickenpalayam (110+)	193	232
3	Pura (36-100)	33	71
4	Kakara (39-81)	73	68
5	Khadar (B1)	144	72
6	Pomberty (32-49)	54	59
7	Sarol (54-95)	213	277
8	Kamliakheri (21-38)	80	195
9	C-24 (black soil)	144	174
10	C-25 (black soil)	119	207
11	P-40 (black soil)	235	205
12	Q-15 (black soil)	107	154
13	Kodad (40-65)	54	103
14	Patancheru (10-20)	73	94
15	Palathurai (15-38)	467	313
	Paired t test ($P=0.05$)=0.404		

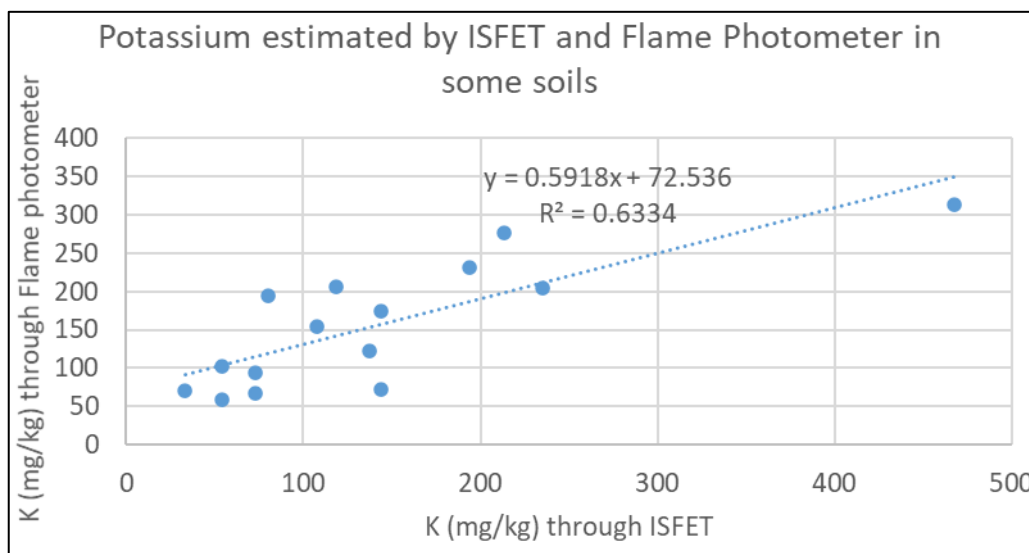


Fig 6: Comparison between potassium estimated by ISFET and Flame Photometer in soils

Comparable results were obtained in the two methods. The results of the paired t test also indicate that there is no significant difference the mean of two results. Comparison of individual data points through regression analysis, though indicates the existence of relationship between the two estimation procedures, the numerical values of potassium obtained by ISFET were quite apart than the corresponding values obtained by Flame photometer.

Conclusion

ISFET has been known for its real time results, robustness, small size, low sample volume and mobility despite of that there are limitations hindering the use in application which must be carefully analysed. The results for pH ISFET was highly significant with the convectional method. Further, improvement in ISFET technology is needed in the direction of enlarging the linearity range especially towards lower end. Presently the linearity range is achieved up to 10^{-4} M Nitrate, however the convention method extracted soil nitrate levels are generally lower than this value. Similar conclusions can

be drawn for potassium. Issues such as drift and linearity range are dealt with by circuit design and software approaches. The stable sensor response is another area that require improvement. In our case it ranged from 5 to 15 minutes. Usually, the sensor response in the order of seconds is required for better throughput.

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